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Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

A RAPID METHOD FOR HYDROCARBON - TYPE DETERMINATION IN SYNTHETIC FUELS

by

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DECEMBER 1978

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 78-114 (TR)

CONTENTS

	Page
ABSTRACT	
INTRODUCTION	1
EXPERIMENTAL	2
Hydrocracking	2
Distillation	2
Deasphalting	2
Hydrocarbon-Type Separation	2
Molecular Weights	2
Sulphur Analysis	2
Molar Absorptivity	2
Use of Detectors	3
RESULTS AND DISCUSSION	3
REFERENCES	5

TABLES

1. Refractive Index of Paraffins	6
2. Calibration Factors for Saturate Fraction	7

FIGURE

1. Hydrocracking and Separation (Schematic)	8
2. Dual Detector System (Schematic)	9

INTRODUCTION

The development of processes for the conversion of bitumens and heavy oils to useful products requires analytical techniques to follow changes in composition. The method currently used in our laboratory (1) to determine hydrocarbon types present in synthetic fuel fractions boiling above 200°C requires one to two working man-days to complete a sample. This procedure is a modification of the US Bureau of Mines - API method (2) for characterization of medium and heavy distillates of bitumen, heavy oils and their processing products. Liquid chromatography on a dual-packed silica-alumina gel column, evaporation of solvents and weighing of samples are involved. Molecular weight determinations are necessary for determination of the aromatic-type distribution on a molar basis. This procedure is not only time consuming, but is susceptible to manual errors.

Equivalent information regarding hydrocarbon-type composition could be provided with a minimum of time and effort by utilizing a dual-detector system consisting of an ultraviolet detector and a refractive index detector in series to monitor the effluent from the chromatographic column. This eliminates time consuming gravimetric determinations which require both solvent evaporation and sample weighing.

The main drawback to the USBM-API method is the time required to complete analysis of a sample. By utilizing the relationship between concentration and refractive index response to saturate compounds; as well as the relationship between ultraviolet absorbance and change of concentration of aromatics, the required information concerning weight percent distribution can be obtained in a shorter time.

This report deals only with the saturate fraction.

EXPERIMENTAL

Hydrocracking

The hydrocracking and separation schematic is shown in Fig. 1.

Hydrocracking was carried out using a one barrel/day pilot plant, the operating details of which have been described elsewhere (3).

Distillation

The light oil hydrocracking product was distilled (ASTM D216-54) to separate the naphtha up to 200°C. The fraction boiling above 200°C was combined with the deasphaltened heavy-oil product in proportion.

Deasphalting

The asphaltene portion of the heavy oil was precipitated by the addition of twenty volumes of pentane to one volume of oil according to a previously described procedure (4).

Hydrocarbon-type Separation

The combined light oil fraction boiling above 200°C and the deasphaltened heavy oil were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics, polar materials, and basic compounds on a dual-packed silica-alumina gel chromatographic column (1,2).

Molecular Weights

The average molecular weights of the various types of molecular structures were determined by vapour pressure osmometry.

Sulphur Analysis

The total sulphur content present in the aromatic fractions was determined coulometrically using the Dohrmann microcoulometer.

Molar Absorptivity

Hydrocarbon-type separations of feed and two samples treated at different hydrocracking severities (pitch conversion 49% and 89%) were

performed as calibration runs. Appropriate fractions representing the aromatic hydrocarbon types were combined, and the solvent evaporated. Molar absorptivities were determined from ultraviolet spectra of known concentrations of these aromatic hydrocarbon types (monoaromatics, diaromatics, polyaromatics) using Beer's Law calculations.

Use of Detectors

The following steps were involved in this procedure:

(1) A refractive index detector was used to detect and quantitate the saturate fraction. Response factors were determined by comparing peak areas with gravimetric results obtained by the modified API-USBM method using samples of Athabasca feed and two hydrocracked products.

(2) An ultraviolet detector was used to detect the aromatic fraction. The aromatic fractions were quantitated using average molar absorptivities calculated from a calibration run.

RESULTS AND DISCUSSION

In this report only the work on quantitating the saturated hydrocarbon fraction is discussed.

The refractive index detector was found to be the most suitable detector for the saturate fraction. Although there would be some separation of saturates with different refractive indices on the column, these differences are not significant (Table 1), and an average refractive index would be obtained over the complete fraction.

As the weight percent of saturates was determined from the response of the refractive index detector, the analysis time was simply the time required for the saturate fraction to be eluted from the column (80 minutes); plus the time required to determine the peak area using calibration curves.

Calibration factors for the saturates were determined by dividing the peak area by the weight of sample.

As can be seen, the calibration factors for the feed and hydrocracked samples do not differ significantly (Table 2). A calibration curve can be drawn for peak areas versus sample sizes and the unknown saturated hydrocarbon concentration associated with a certain peak area read directly from the graph.

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TABLE 1

Refractive Index of Paraffins

Compound	Index of Refraction
2,3-dimethylbutane	1.3750
2,2-dimethylbutane	1.3688
2,4-dimethylpentane	1.3815
3-methylhexane	1.3886
2,2,5-trimethylhexane	1.3997
n-undecane	1.4172
n-hexadecane	1.4345
2,2,4-trimethylpentane	1.3890

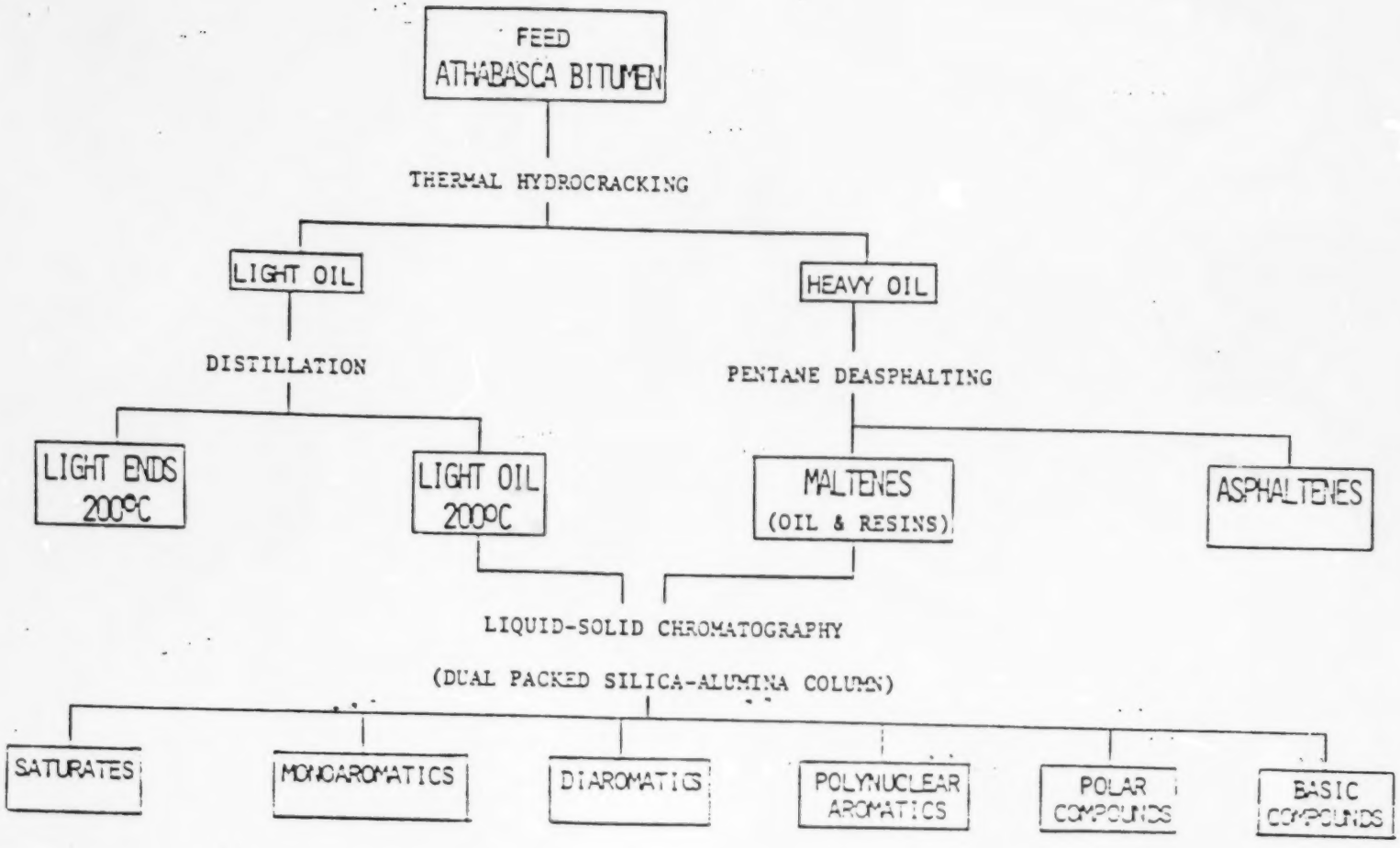
Average Deviation = 0.0171

TABLE 2

Calibration Factors for Saturate Fraction

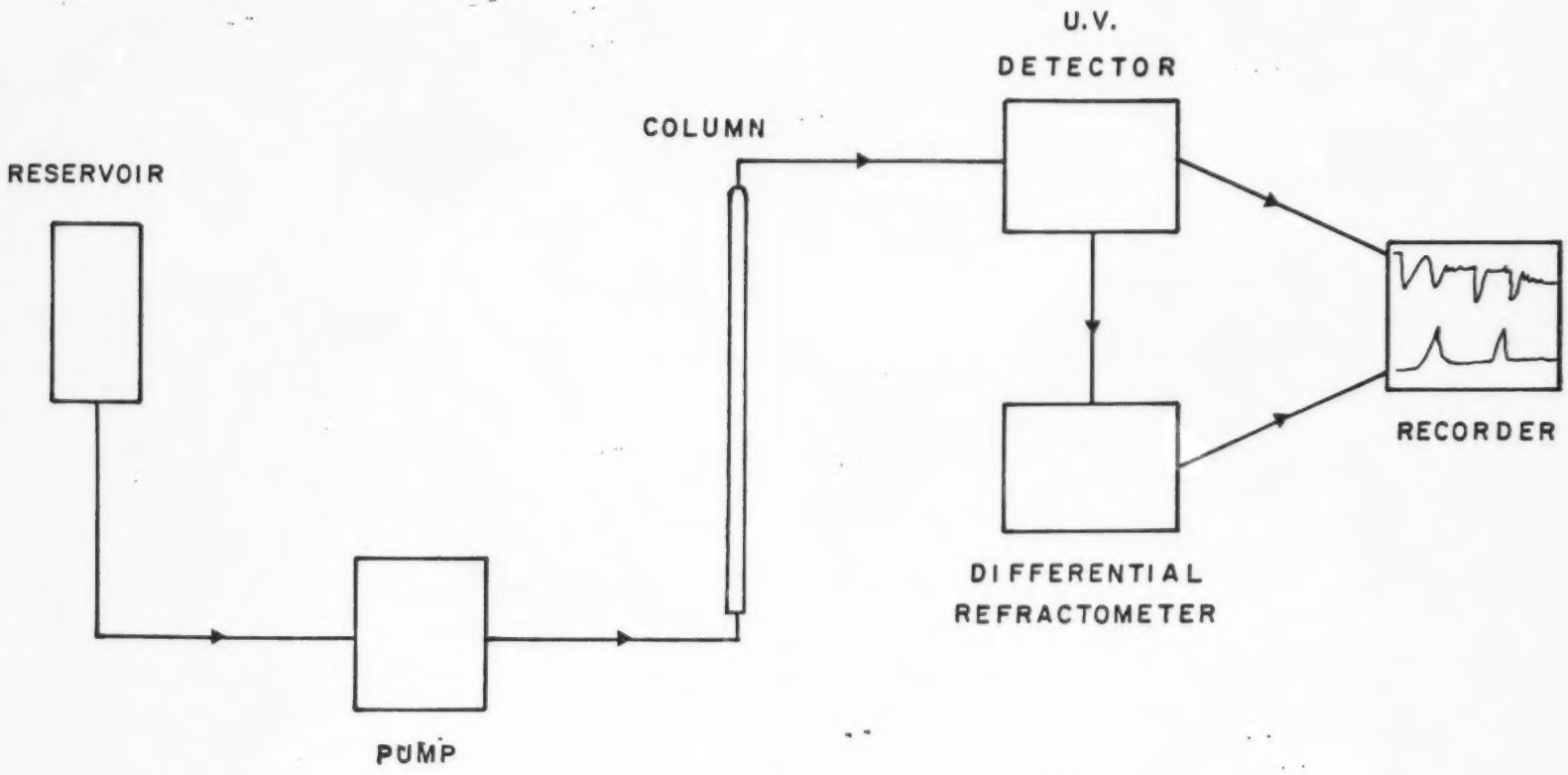
Sample	Peak Area $(cm)^2$	Weight of Fraction mg	Calibration Factor cm^2/g	Saturate Content wt %
Feed	30.61	357.6	85.59	24
Medium Hydrocracked	36.96	397.6	88.53	28
Severely Hydrocracked	44.30	477.8	92.71	36

Average deviation calibration factor = 2.40



HYDROCRACKING AND SEPARATION (SCHEMATIC)

FIGURE I



Schematic of Dual Detector System

FIGURE-2